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Conductivity and atomic structure of isolated multiwalled carbon nanotubes

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Abstract. We report associated high resolution transmission electron microscopy (HRTEM) and transport measurements on a serie of isolated multiwalled carbon nanotubes. HRTEM observations, by revealing relevant structural features of the tubes, shed some light on the variety of observed transport behaviors, from semiconducting to quasi-metallic type. Non Ohmic behavior is observed for certain samples which exhibit "bamboo like" structural defects. The resistance of the most conducting sample exhibits a pronounced maximum at 0.6 K and strong positive magnetoresistance.

We report the results of simultaneous investigations of the electric properties and structure of nanotubes in the transmission electron microscope. The technique used for isolating an individual nanotube is qualitatively different from the other studies [1, 2, 3]. It allows studying in HRTEM the structure of the nanotube. The method consists in the following: a focused laser beam "shakes off" a nanotube from the target onto a sample with a Si_3N_4 membrane covered with a metal film [4, 5]. A submicron width slit about 100 μm in length has previously been cut in the membrane by focused ion beam; the nanotube connects the edges of the slit (see Fig. 1) and shorts the electric circuit whose resistance was over $1 \text{ G}\Omega$ before the nanotube was "shaken off". In the following we successively discuss electron microscopy observations and transport measurements on a family of tubes indexed as Au_N , Sn_N , Bi_N depending on the nature of the used metal contact.

Most investigated nanotubes cannot be described only as perfect sets of coaxial cylinders, but exhibit defects which can affect the transport mechanisms. In particular a defect so called bamboo defect in the literature [6], has been identified in many cases: the inner shells of the nanotube are interrupted and separated by fullerene semi-spheres while the outer shells remain continuous, (see Fig. 1A). The presence of such defects is indicated in Table 1. We will see that the presence of these defects affects transport properties when there exists a possibility of conduction between the outer and inner shells.

We have tentatively separated the different temperature dependences observed depicted in Fig. 2 in 3 main types of behavior: semi-conducting, (type I_A, I_B) and quasi-metallic, (type II) which can be characterized by the ratio α_R between the values of the resistance at 100 K and 293 K, it is above 1000 for I_A, of the order of 100 for I_B and below 10 for type II tubes.

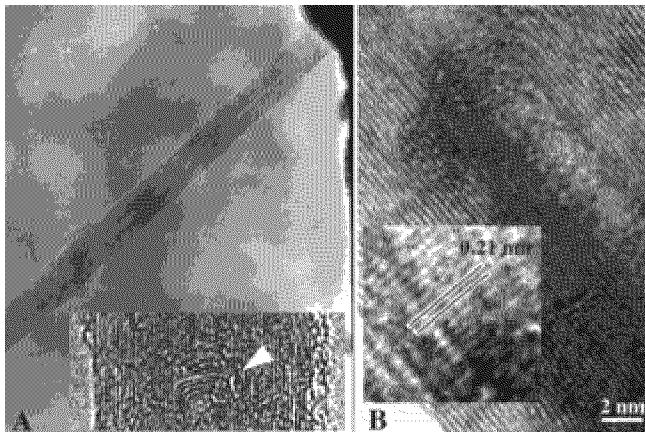


Fig 1. HRTEM on studied samples: A—partial view of a connected nanotube (only one metallic pad is visible). Some carbonaceous material, due to electron damage during observation, is visible on the surface of the nanotube. Inset: HRTEM of a bamboo defect. B—HRTEM picture of Sn2 tube showing evidence of ordered stacking of zig-zag type shells.

Table 1. Resistance and structural parameters of various nanotubes. $\Phi_{\text{out,in}}$ and L are respectively the external, internal diameters and length between the 2 metallic contacts.

| Sample name | $\Phi_{\text{out,in}}$ (nm) | # of shells | L (μm) | Bamboo defects | $R (\Omega)$ 293 K | α_R | Type |
|-------------|-----------------------------|-------------|---------------------|----------------|--------------------|------------|----------------|
| Au1 | 25, 7 | 26 | 2.1 | No | $1.0 \cdot 10^6$ | $> 10^3$ | I _A |
| Sn2 | 40, 3 | 55 | 0.33 | No | $2.1 \cdot 10^4$ | $> 10^5$ | I _A |
| Sn5 | 25, 5 | 29 | 0.45 | Yes | $2.5 \cdot 10^6$ | $> 10^3$ | I _A |
| Au2 | 16, 5 | 16 | 0.36 | Yes | $6.7 \cdot 10^5$ | 140 | I _B |
| Sn10 | 7, 2 | 7 | 0.35 | Yes | $5.8 \cdot 10^6$ | 86 | I _B |
| Sn11 | 13, 7 | 9 | 0.17 | Yes | $1.8 \cdot 10^6$ | 40 | I _B |
| Bi4 | 12, 4 | 11 | 0.4 | Yes | $2.8 \cdot 10^4$ | 1.2 | II |
| Au3 | 25, 3 | 29 | 0.17 | No | $1.9 \cdot 10^3$ | 4 | II |
| Au4 | 26, 5 | 31 | 0.33 | No | $2.0 \cdot 10^5$ | 6 | II |

Type I_A and I_B tubes exhibit a semiconducting behavior between 300 K and 200 K, with approximative exponentially activated temperature dependence of the resistance (see Fig. 2). All the gap values lie between 2000 and 3000 K, this reasonably excludes some contribution of the contact resistance to these gaps which are similar to values in amorphous carbon [7]. For each type I_B tube, a saturation of the resistance around $10^8 \Omega$ is observed below 100 K. This saturation does not exist for type I_A samples. It is striking that all these I_B tubes contain one “bamboo” defect and are also characterized by their strongly non linear $I-V$ characteristics below 100 K [10]

Type II tubes exhibit a “quasi-metallic” behavior. Their resistances increase more slowly than exponentially at low temperature, varying approximatively like $1/T^x$ with $x = 0.5$ for Au3 and $x = 2$ for Au4 (see Fig. 2), a slower increase was observed for Bi5 [4]. We never see any increase of resistance at high temperature similar to what is observed in “bulk” samples of SWNT [8]. Note however that this type of true “metallic” behavior has only been recorded so far in “bulk” samples or ropes of SWNT and has never been reported for isolated nanotubes. On the Au3 sample we could also perform very low temperature transport measurements, shown in Fig. 3. The $R(T)$ curve

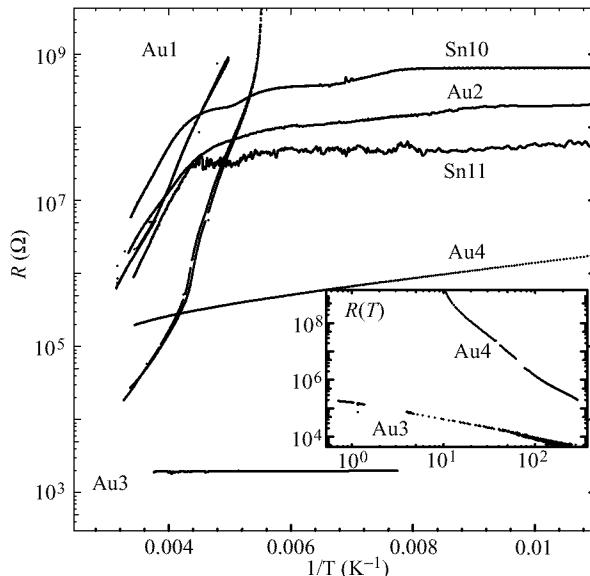


Fig 2. High temperature resistance of the tubes, showing evidence of semiconducting behavior for most of them. Inset: Resistance of Au4 and Au3 samples on a wider temperature range, which exhibits power law increase at low temperature.

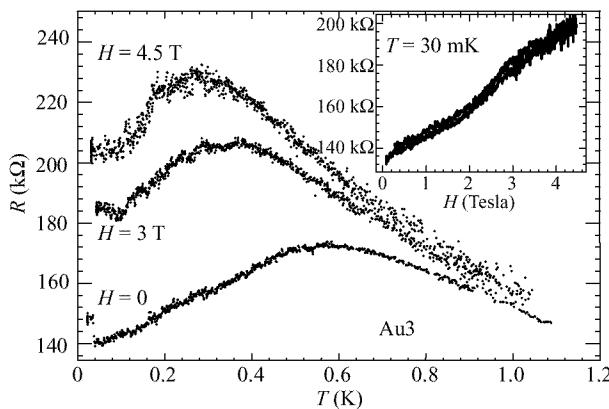


Fig 3. Low temperature resistance and in inset, magnetoresistance of the Au3 sample.

exhibits a broad maximum around 0.6 K. The amplitude and position of this maximum vary drastically with the magnitude of magnetic field applied perpendicularly to the tube axis. It shifts to lower temperature with increasing magnetic field and reaches higher resistance values. Accordingly, one observes a large positive magneto-resistance approximatively linear in magnetic field (with a 50% increase for an applied field of 4 T.) To our knowledge it is the first time that such remarkable features have been observed in the resistance measurements of nanotubes.

One important issue for understanding transport properties of these nanotubes is the separation between the contribution of the most external shell, which is the only one directly connected to the metallic pads, and the possible contributions of internal shells. This is determined by the ratio $\eta = R_{\text{ext}}/R_t$ between the resistance R_{ext} of this external

shell and the resistance R_t connecting this shell to internal shells. We expect the value of R_t to drastically depend on the spatial correlation between atomic positions in adjacent graphite planes which determine the overlap between π orbitals perpendicular to these planes. The value of η may then fluctuate a lot between different nanotubes and also depend on temperature. We naturally expect that $\eta \ll 1$ for (metallic) type II nanotubes. The combination of HRTEM observations and transport measurements suggests that $\eta \ll 1$ also for type I_A nanotubes. One convincing example is the Sn2 sample which, according to HRTEM observations, contains many zig-zag shells arranged in a nearly perfect graphitic order. According to theoretical predictions [9], depending of their diameter, we can expect that 1/3 of these shells are metallic. However the measured temperature dependence of the resistance indicates a semiconducting behavior. These two results can be reconciled if transport takes place in the semiconducting external shell of the tube and if there is no possibility of conduction through internal metallic shells.

The situation is different for type I_B samples, where Fig. 2 indicate a residual tunneling conductivity at low temperature which scales approximatively like the surface of the inner section of the tube. A possible explanation of these findings could be tunneling on a metallic inner shell of the tube, behaving as a Coulomb island, separated from the metallic pads by external shells which are insulating at low temperature but however offer the possibility of electron transfer through high but finite tunneling resistance R_t . HRTEM observations reveal a complex situation with the existence of “bamboo” like defects [10].

In conclusion, simultaneous HTREM and resistance measurements performed on the same characterized samples, highlight the importance of internal structural defects when compared to the helicity parameters, in the mechanism of electron conductivity. We have also shown that the outer shell determines the resistance for most insulating or conducting tubes. Specific “bamboo” type defects could be identified which are fundamental for the understanding of intermediate behavior, where internal shells contribute to electronic transport through tunnel junctions. We have finally demonstrated that measuring transport properties of nanotubes is specially interesting at very low temperatures with the existence of an anomaly in the temperature dependence, highly sensitive to the strength of magnetic field.

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